Effects of Time and Temperature of Steeping on the Soluble Constituents of Sicilian and Domestic Sumacs

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Introduction

In preparing sumac extract from the leaves, manufacturers recognize that the total time between the start of the leaching process and completion of evaporation of the extract should be as short as possible. Published data, however, dealing with the effects of time and temperature of extraction on the quality of the extract are meager and are concerned only with Sicilian sumac.

Parker and Procter,[5] using a Procter extractor, investigated the effect of different temperatures in the extraction of tanning materials for analysis. In studying sumac, the maximum quantity of tannin, 20.3 per cent, was obtained at 50° to 60° C. The maximum purity of the extractive was obtained at approximately the same temperature. Above 60° C. the tannin value decreased and was only 16.6 per cent at 90° to 100° C. Non tannins increased regularly from 17.8 per cent to 24.0 per cent as the temperature of extraction was increased from that of the room to boiling. The color of the extractives, as measured with a Lovibond tintometer, decreased slightly as the temperature increased from 15° to 40° C., but then increased as long as the temperature increased. After examining several methods for the extraction of sumac for analysis, Parker and Winch[6] reported that, although soaking overnight was necessary for concordant results, soaking for two nights resulted in a loss of from 0.8 to 2.5 per cent of tannin if the temperature exceeded 17° C. They also stated that, in making sumac extract commercially, the yield of tannin was seriously affected both by the time the water was left in contact with the sumac leaf and the time that elapsed between extraction and concentration.

Parker and Gilman[4] found that "scalding" sumac before extraction by pouring 200 cc. of boiling water on the material in a Procter extractor resting in a boiling water bath, then allowing the bath and contents to cool to room temperature overnight, lowered the tannin content by about 2 per cent with no change in non tannins, as compared with unscalded material. These investigators also showed[4] that soaking sumac for 40 hours before extraction instead of the customary 18 hours resulted in a

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loss of tannin and an increase in non tannins, but these changes were pre vented by a preliminary heating for 1 to 1.5 hours at 103° C. before the 40 hour soak, presumably because of sterilization of the material.

The investigation reported here was not concerned with the optimum temperature for an analytical extraction but rather with the effect of heating under conditions similar to those prevailing during leaching in the production of sumac extract. Specifically, it dealt with (1) the maximum time and (2) the maximum temperature that might be used for soaking sumac leaves in water without excessive loss of tannin and lowering of the purity of the extract, and (3) the effect of heating on the color of leather produced from heated sumac. The data obtained also afford a comparison of the stability under such conditions of imported Sicilian sumac and the three principal domestic species found in the eastern States.

Description of Samples and Procedure

A preliminary series of tests were made with two species of sumac, dwarf sumac (*Rhus copallina* L.) and white sumac (*Rhus glabra* L.)

The dwarf sumac was collected in the southern part of Virginia in 1941, dried at once by artificial heat, then flailed to separate stems and leaves. The sample consisted principally of leaflets. The white sumac consisted of entire leaves hand-picked in 1942 in the southeastern part of Iowa and dried in the shade at ordinary temperatures.

A final series of tests were made in which the following four species were used: Dwarf sumac, white sumac, staghorn sumac (*R. typhina* Torn.), and Sicilian sumac (*R. coriaria* L.). For this series, dwarf sumac leaves were used that had been collected at Beltsville, Md. in 1943 and dried in the air. They were air-elutriated by machine to remove most of the petioles. The white sumac consisted of leaflets collected near Hagerstown, Md. in 1943 and dried in the air. All petioles and most of the rachises were removed by air-elutriation. The staghorn sumac, collected in the vicinity of Wyndmoor, Pa. in 1944, consisted of leaflets that had been separated by hand from the petioles-rachises as soon as the leaves were air dry. The Sicilian sumac, although imported several years previously, was taken from the most recent shipment of ground leaf available. It was used without any treatment except removal by hand of the larger pieces of stems.

The procedure for the tests was as follows: Leaf material was steeped in water at four temperatures, namely, 30°, 50°, 70°, and 90° C., for time periods of 1, 2, 3, and 5 days in the preliminary series and 6, 12, 24, and 48 hours in the final series.

For a test, the quantity of material needed to give four grams of tannin per liter in the analytical solution from an unheated portion of leaflets was weighed into a beaker and wet with two or three times its weight of water at the temperature being used in the particular test. The material was transferred at once to a Clarke and Frey[2] type of extraction tube with the rubber delivery tube in the reflux position and the bottom of the vapor tube closed by a rubber stopper. Sufficient water was added to make the final weight of water in the tube approximately five times that of the sample. After the leaf material had settled, the supernatant liquid was about half the total volume. This proportion of liquid to solid was greater than would be used in one filling of a leach tank in commercial extraction but less than the total volume that would be used. The tube was then placed in a constant temperature water bath* and maintained within about 0.1 degree of the desired temperature throughout the test period. For each species of sumac, all samples to be tested at the same temperature were heated and analyzed at the same time. The required number of portions were weighed into beakers at the same time and were wet, transferred to tubes, and placed in the constant temperature bath at different times, adjusted so that all the heating periods would end simultaneously. At the end of the heating periods, all tubes were removed from the bath, transferred directly to an extraction battery[2] and extracted and analyzed by the Official methods of the American Leather Chemists Association.[1] With each set, one portion of leaves was extracted immediately, without steeping with the others, for a control.

Some difficulty was experienced in the extraction of the staghorn and Sicilian sumacs. To minimize this a layer of purified quartz sand about one-half inch deep was spread over the cotton in the bottom of the extraction tube before adding the sumac.

In addition to the usual tannin analysis, determinations were made of reducing and total sugars, pH value and color. The color of each soluble solids solution was measured by determining transmission at wave lengths of 436, 546 and approximately 620 millimicrons. Skivers were tanned with the various total solids solutions by the method of Riethof[7], except that sheepskin rather than cowhide skivers were used. Reflectance measurements were made on the tanned skivers at the wave lengths noted above. Complete reflectance or transmission curves for the visible region were made on a few of the solutions and skivers. All tests were made in duplicate throughout, and the results reported in the tables are averages of the duplicates except for a few determinations lost during extraction.

In the preliminary series, the portions steeped at room temperature, 21° to 27° C., developed considerable mold during the 3 and 5 day steeping periods. To retard mold growth, all portions for the 30° C. tests in the final series were treated at the start of the steeping period with a few small crystals of 2-chloro-5-hydroxytoluene. This did not prevent mold growth entirely, however, for mold developed in all 48 hour tests, and the amount

* A Reed-Churchill extractor[3] was excellent for this purpose.

TABLE I

Effect of Variations in Time and Temperature of Steeping on the Composition of *Rhus copallina* Leaflets

Results on Moisture-Free Basis

Temperature of Heating	Time of Heating	Insolubles	Soluble Solids	Non Tannins	Tannin	Purity of Extractive*	Sugars: Reducing	Sugars: Non-Reducing	Sugars: Total	pH of Soluble Solids
°C.	Hours	%	%	%	%	%	%	%	%	
30	0	1.7	51.9	18.5	33.4	64.3	2.9	2.2	5.1	4.0
"	6	1.5	52.2	19.0	33.2	63.6	3.4	1.8	5.2	4.0
"	12	1.2	52.4	19.1	33.3	63.6	3.6	1.7	5.3	4.0
"	24	1.2	52.0	19.5	32.5	62.5	3.7	1.5	5.2	4.0
"	48	1.1	51.5	20.6	30.9	60.0	3.8	1.6	5.4	3.9
50	0	1.6	51.5	18.7	32.8	63.7	3.0	2.2	5.2	4.0
"	6	1.1	51.9	19.1	32.8	63.2	3.2	1.9	5.1	4.0
"	12	1.3	51.4	19.5	31.9	62.1	3.3	1.9	5.2	4.0
"	24	1.5	51.6	20.1	31.5	61.0	3.2	1.7	4.9	4.0
"	48	1.1	52.6	21.2	31.4	59.6	3.4	1.7	5.1	4.0
70	0	1.7	52.1	18.8	33.3	63.9	3.2	2.1	5.3	4.1
"	6	1.7	52.0	19.3	32.7	62.8	3.2	1.9	5.1	4.0
"	12	1.5	51.7	19.7	32.0	61.9	3.3	1.8	5.1	4.0
"	24	1.4	51.7	20.4	31.3	60.5	3.2	1.9	5.1	3.9
"	48	1.8	51.7	21.7	30.0	58.0	3.3	1.7	5.0	3.8
90	0	1.8	52.3	19.0	33.3	63.6	2.8	2.4	5.2	4.0
"	6	1.7	51.8	21.0	30.8	59.4	3.0	2.1	5.1	3.8
"	12	2.2	52.2	22.8	29.4	56.3	3.2	1.9	5.1	3.8
"	24	2.8	52.2	24.7	27.5	52.7	3.3	1.9	5.2	3.7
"	48	3.1	51.8	27.3	24.5	47.3	3.9	1.8	5.7	3.6

*Purity of extractive is 100 times the tannin value divided by soluble solids.

TABLE II

EFFECT OF VARIATIONS IN TIME AND TEMPERATURE OF STEEPING ON THE COMPOSITION OF *Rhus coriaria* LEAVES

Results on Moisture-Free Basis

Temperature of Heating	Time of Heating	Insolubles	Soluble Solids	Non Tannins	Tannin	Purity of Extractive*	Sugars: Reducing	Sugars: Non-Reducing	Sugars: Total	pH of Soluble Solids
°C.	Hours	%	%	%	%	%	%	%	%	
30	0	2.2	49.5	19.8	29.7	60.0	3.3	1.2	4.5	4.5
"	6	1.5	49.9	20.2	29.7	59.5	3.5	0.9	4.4	4.5
"	12	1.7	50.3	20.3	30.0	59.6	3.5	0.8	4.3	4.5
"	24	1.6	50.4	20.9	29.5	58.5	3.4	0.9	4.3	4.5
"	48	1.8	50.1	21.6	28.5	56.9	3.5	1.0	4.5	4.5
50	0	2.0	49.7	19.8	29.9	60.2	3.4	1.1	4.5	4.4
"	6	1.6	50.2	20.2	30.0	59.8	3.4	1.0	4.4	4.4
"	12	1.9	50.2	21.0	29.2	58.2	3.5	0.9	4.4	4.4
"	24	1.8	50.4	21.8	28.6	56.7	3.5	0.9	4.4	4.4
"	48	1.5	50.9	22.4	28.5	56.0	3.5	1.0	4.5	4.4
70	0	2.0	50.0	20.0	30.0	60.0	3.6	0.9	4.5	4.3
"	6	1.9	49.8	20.5	29.3	58.8	3.4	1.0	4.4	4.3
"	12	2.3	50.0	21.2	28.8	57.6	3.5	0.9	4.4	4.3
"	24	2.4	50.1	22.1	28.0	55.9	3.5	0.8	4.3	4.2
"	48	2.8	49.7	23.4	26.3	52.9	3.6	0.8	4.4	4.2
90	0	1.5	50.5	20.0	30.5	60.4	3.5	0.7	4.2	4.2
"	6	2.9	50.2	23.3	26.9	53.6	3.5	0.7	4.2	4.0
"	12	3.2	50.9	25.6	25.3	49.7	3.6	0.7	4.3	4.0
"	24	3.1	51.9	28.0	23.9	46.1	3.8	0.6	4.4	3.9
"	48	3.0	52.3	30.1	22.2	42.4	3.9	0.6	4.5	3.8

*Purity of extractive is 100 times the tannin value divided by soluble solids

TABLE III

EFFECT OF VARIATIONS IN TIME AND TEMPERATURE OF STEEPING ON THE COMPOSITION OF *Rhus glabra* LEAFLETS

Results on Moisture-Free Basis

Temperature of Heating	Time of Heating	Insolubles	Soluble Solids	Non Tannins	Tannin	Purity of Extractive*	Sugars: Reducing	Sugars: Non-Reducing	Sugars: Total	pH of Soluble Solids
°C.	Hours	%	%	%	%	%	%	%	%	
30	0	1.3	49.4	20.2	29.2	59.1	4.1	1.8	5.9	4.3
"	6	1.1	49.4	20.6	28.8	58.3	4.4	1.6	6.0	4.2
"	12	1.0	49.5	20.7	28.8	58.2	4.4	1.7	6.1	4.2
"	24	0.8	49.4	21.9	27.5	55.7	4.5	1.7	6.2	4.1
"	48	0.8	49.7	23.5	26.2	52.7	4.8	1.5	6.3	4.0
50	0	1.9	48.8	20.2	28.6	58.6	4.1	1.9	6.0	4.4
"	6	1.4	48.7	20.5	28.2	57.9	4.3	1.5	5.8	4.3
"	12‡	1.5	49.5	21.6	27.9	56.4	4.3	1.6	5.9	4.2
"	24	1.2	49.6	22.6	27.0	54.4	4.5	1.6	6.1	4.1
"	48	1.3	50.0	24.0	26.0	52.0	4.5	1.5	6.0	4.1
70	0	1.5	48.9	19.9	29.0	59.3	4.2	1.7	5.9	4.3
"	6	1.5	48.2	20.2	28.0	58.1	4.1	1.6	5.7	4.2
"	12	1.9	48.4	21.1	27.3	56.4	4.2	1.7	5.9	4.1
"	24‡	2.0	48.5	21.9	26.6	54.8	4.2	1.7	5.9	4.1
"	48	2.2	48.8	23.0	25.8	52.9	4.2	1.7	5.9	4.1
90	0	1.8	48.5	20.2	28.3	58.4	3.9	1.9	5.8	4.3
"	6	2.7	48.6	22.5	26.1	53.7	4.2	1.6	5.8	4.0
"	12	2.5	49.0	23.5	25.5	52.0	4.2	1.3	5.5	3.9
"	24	2.7	50.1	25.6	24.5	48.9	4.4	1.2	5.6	3.9
"	48	3.3	50.9	28.2	22.7	44.6	4.7	1.4	6.1	3.8

*Purity of extractive is 100 times the tannin value divided by soluble solids.

‡Single determination; one was lost during extraction.

TABLE IV

EFFECT OF VARIATIONS IN TIME AND TEMPERATURE OF STEEPING ON THE COMPOSITION OF *Rhus typhina* LEAFLETS

Results on Moisture-Free Basis

Temperature of Heating	Time of Heating	Insolubles	Soluble Solids	Non Tannins	Tannin	Purity of Extractive*	Sugars: Reducing	Sugars: Non-Reducing	Sugars: Total	pH of Soluble Solids
°C.	Hours	%	%	%	%	%	%	%	%	
30	0	2.0	49.4	22.2	27.2	55.1	5.2	1.5	6.7	4.4
"	6	1.8	49.4	21.8	27.6	55.9	5.2	1.4	6.6	4.4
"	12	1.6	49.7	22.3	27.4	55.1	5.2	1.5	6.7	4.3
"	24	1.6	49.7	22.5	27.2	54.7	5.1	1.6	6.7	4.3
"	48	1.3	49.8	23.8	26.0	52.2	5.0	1.5	6.5	4.1
50	0	1.7	49.7	22.5	27.2	54.7	4.6	2.0	6.6	4.4
"	6	1.8	49.5	22.4	27.1	54.7	4.9	1.5	6.4	4.3
"	12	1.9	49.3	22.7	26.6	54.0	4.9	1.4	6.3	4.3
"	24	1.7	49.9	23.0	26.9	53.9	4.9	1.5	6.4	4.2
"	48	1.9	49.8	23.2	26.6	53.4	4.9	1.4	6.3	4.2
70	0	1.6	50.0	22.7	27.3	54.6	...	...	6.6	4.3
"	6	1.2	50.1	23.4	26.7	53.3	4.9	1.3	6.2	4.2
"	12	1.8	50.7	24.5	26.2	51.7	4.9	1.4	6.3	4.1
"	24‡	1.9	51.8	25.7	26.1	50.4	4.9	1.3	6.2	4.1
"	48‡	2.1	52.8	27.7	25.1	47.5	5.0	1.3	6.3	4.0
90	0	1.2	49.8	22.7	27.1	54.4	5.0	1.4	6.4	4.4
"	6	3.0	52.0	27.6	24.4	47.0	4.6	1.8	6.4	4.1
"	12‡	2.8	53.2	29.2	24.0	45.1	4.9	1.7	6.6	4.0
"	24	3.3	53.3	30.5	22.8	42.8	5.2	1.5	6.7	3.9
"	48	3.1	53.9	31.4	22.5	41.7	5.8	1.2	7.0	3.8

*Purity of extractive is 100 times the tannin value divided by soluble solids.
‡Single determination; one was lost during extraction.

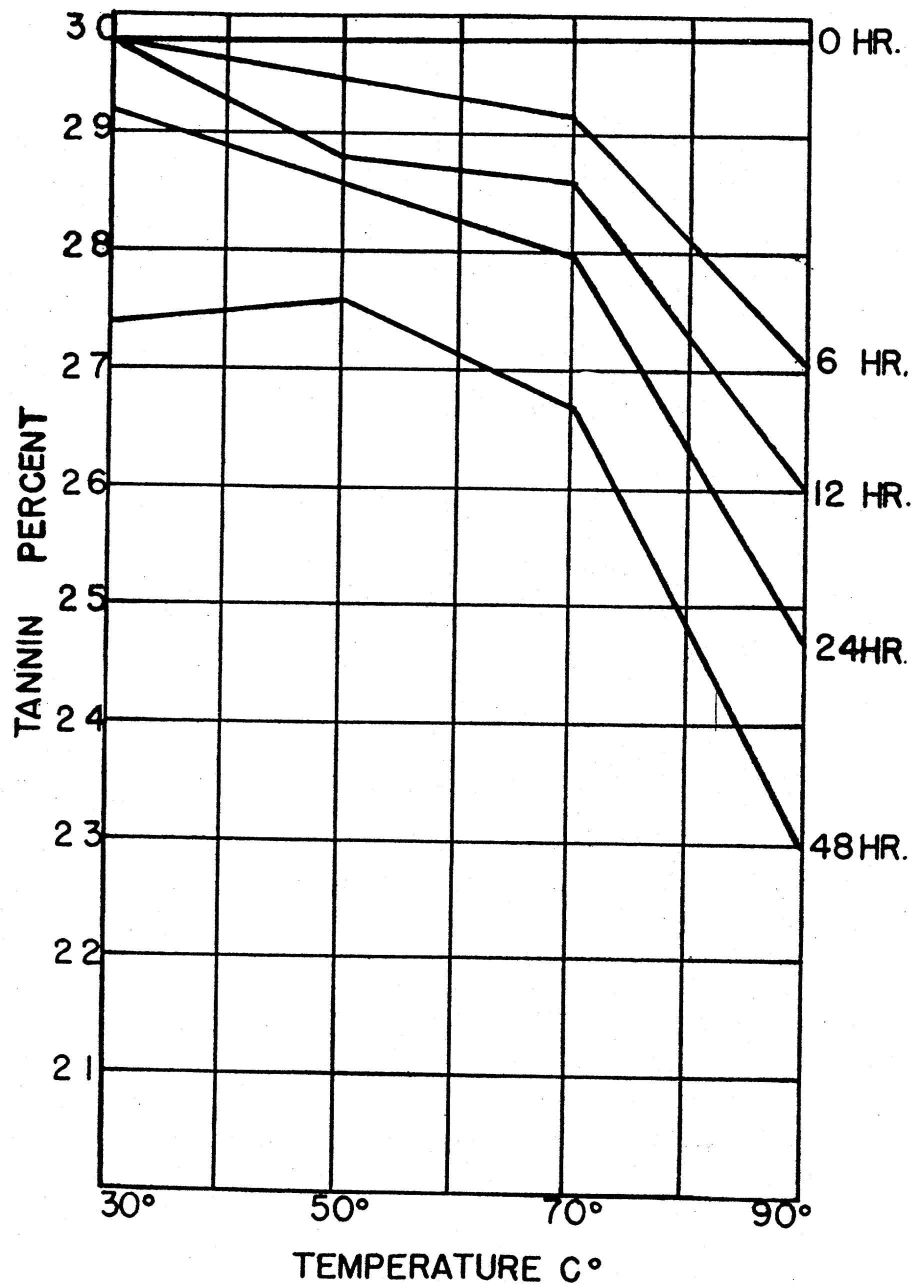

FIGURE I. Variation in tannin content of sumac leaves with temperature of steeping. Average values for four species of sumac steeped for 6, 12, 24, and 48 hours.

TABLE V

Analysis of Variance of Analytical Data Obtained in Studies of the Effect of Variations in Time and Temperature of Steeping Sumac

Source of Variation	Degrees of Freedom	Mean Squares for							
		Insol-ubles	Soluble Solids	Non Tannins	Tannin	Reducing Sugar	Non-Reducing Sugar	Total Sugar	pH
Species	3	2.1897**	39.3489**	91.4231**	164.4383**	18.7668**	5.1148**	26.1581**	0.7603**
Temperature	3	13.8481**	11.0232**	180.0892**	103.7279**	0.3240*	0.0221	0.2735**	0.8723**
Time	3	0.2645	3.4876**	61.7728**	36.3595**	0.4416**	0.0701	0.1937**	0.1593**
Interaction: Species x temperature	9	0.2702	4.6871**	6.0221**	1.3623**	0.0990	0.1377	0.1325**	0.0393*
Interaction: Species x time	9	0.0468	0.5359	0.4135**	0.7142**	0.0147	0.0125	0.0150	0.0035
Interaction: Temperature x time	9	0.3010	0.7555*	4.4163**	2.3975**	0.1441	0.0238	0.0934*	0.0052
Interaction: Species x temperature x time	27	0.0981	0.2171	0.4032**	0.3785*	0.0278	0.0204	0.0178	0.0053
Analyses on different days—Error	12	0.1464	0.2503	0.0717	0.1515	0.0587	0.0653	0.0219	0.0112
Duplicates on same day	61	0.0218	0.1101	0.0405	0.0758	0.0026	0.0164	0.0165	0.0002

*—Significant at 5 per cent point.

**—Significant at 1 per cent point.

was sufficient to be visible on the surface of the solutions of dwarf and white sumac.

Although the work reported here was concerned primarily with the effect of temperature during steeping, some data on the effect of dry heat were obtained in order to show the role of water during heating. For this purpose portions of leaf material were weighed into beakers and heated in an electric oven at 100° to 102° C. for 24 or 48 hours. Then the material was wet with water, transferred to an extraction tube and extracted and analyzed at the same time as the samples in the 90° C. wet-heat tests.

Results

The results for the final series of tests, involving heating periods up to 48 hours, will be discussed first because they were more complete than the first series, both in number of species examined and number of determinations made on each. The data are presented in Tables I to IV inclusive.

Tannin: Tannin in all four species decreased as either temperature or time was increased. After 48 hours at 90° C., the decrease in tannin was approximately 26 per cent of the original value for *R. copallina,* 27 for *R. coriaria,* 20 for *R. glabra,* and 17 for *R. typhina*. An analysis of variance[8], using the results at zero time to obtain the error term, is given in Table V. It shows highly significant differences due to species, temperature, time, and interactions between any two of these factors.

Curves showing variation in per cent tannin with temperature for the different time periods have approximately the same general form, although those for R. *copallina* are farther apart and those for *R. typhina* are closer together and show less spread at 90° C. than do the curves for the other two species. Curves based on average values for all four species are given in Figure I to show the general behavior of sumac on steeping. The curves, however, do not exactly represent the changes for each species.*

In Figure II the percentages of tannin for *R. coriaria* and also the logarithms of percentage tannin for the 90° test are plotted against time of heating. If tannin were a single chemical compound its destruction by heat would be expected to be a first order reaction, and a curve showing variation of logarithm of tannin concentration with time should be a straight line. The line so obtained is not straight, indicating that the reaction slows somewhat as it progresses. Such behavior might be expected, for the system under consideration is complex. Tannin, as determined in this work, is not a single compound, but a group of related compounds which on heating may decompose at different rates. Also, since the whole leaf was present, other reactions may have occurred; for example, there may have been a liberation

* An analysis of variance of the deviations of tannin values for each species from the average values for all four species gave the following mean squares for interaction: Species x temperature, 0.68; species x time, 0.36; species x temperature x time, 0.19; and error, 0.06. The corresponding degrees of freedom were 9, 9, 27, and 12.

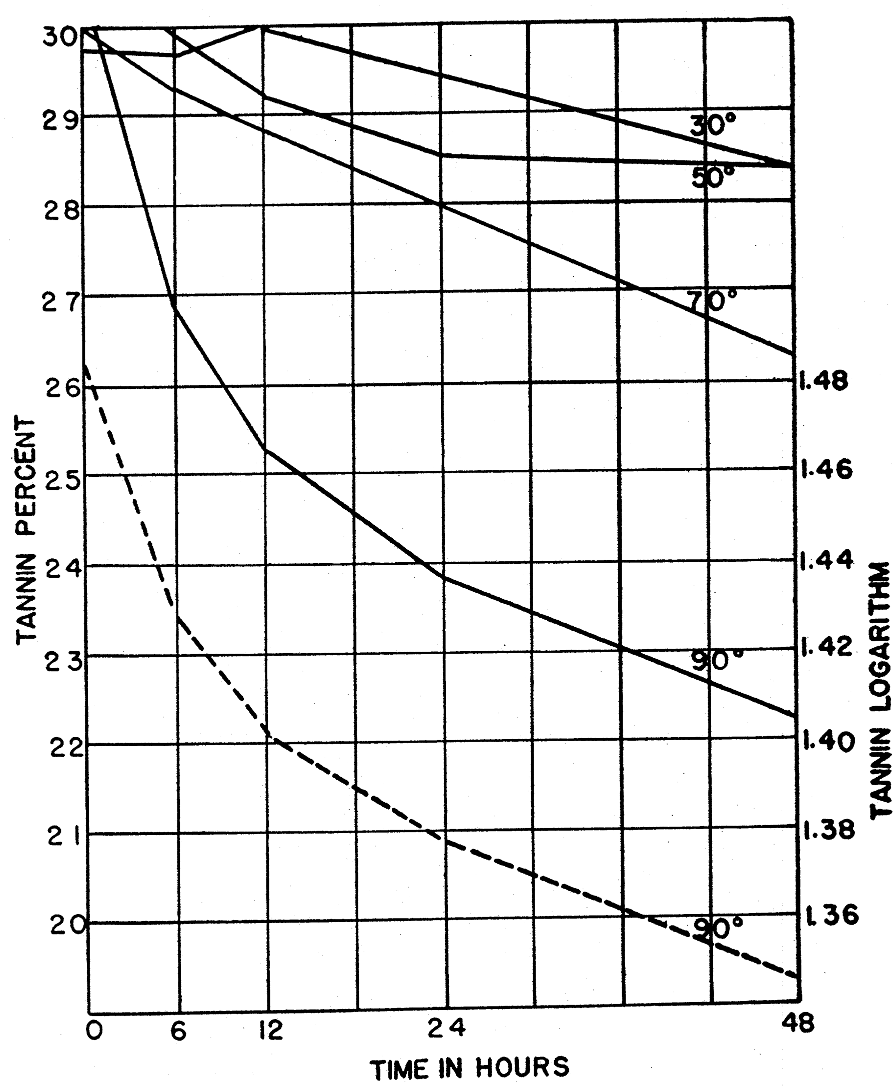

FIGURE II. Variation in tannin content of *Rhus coriaria* leaves with time of steeping at four temperatures. Solid lines are percentages of tannin; broken line is logarithm of percentage tannin.

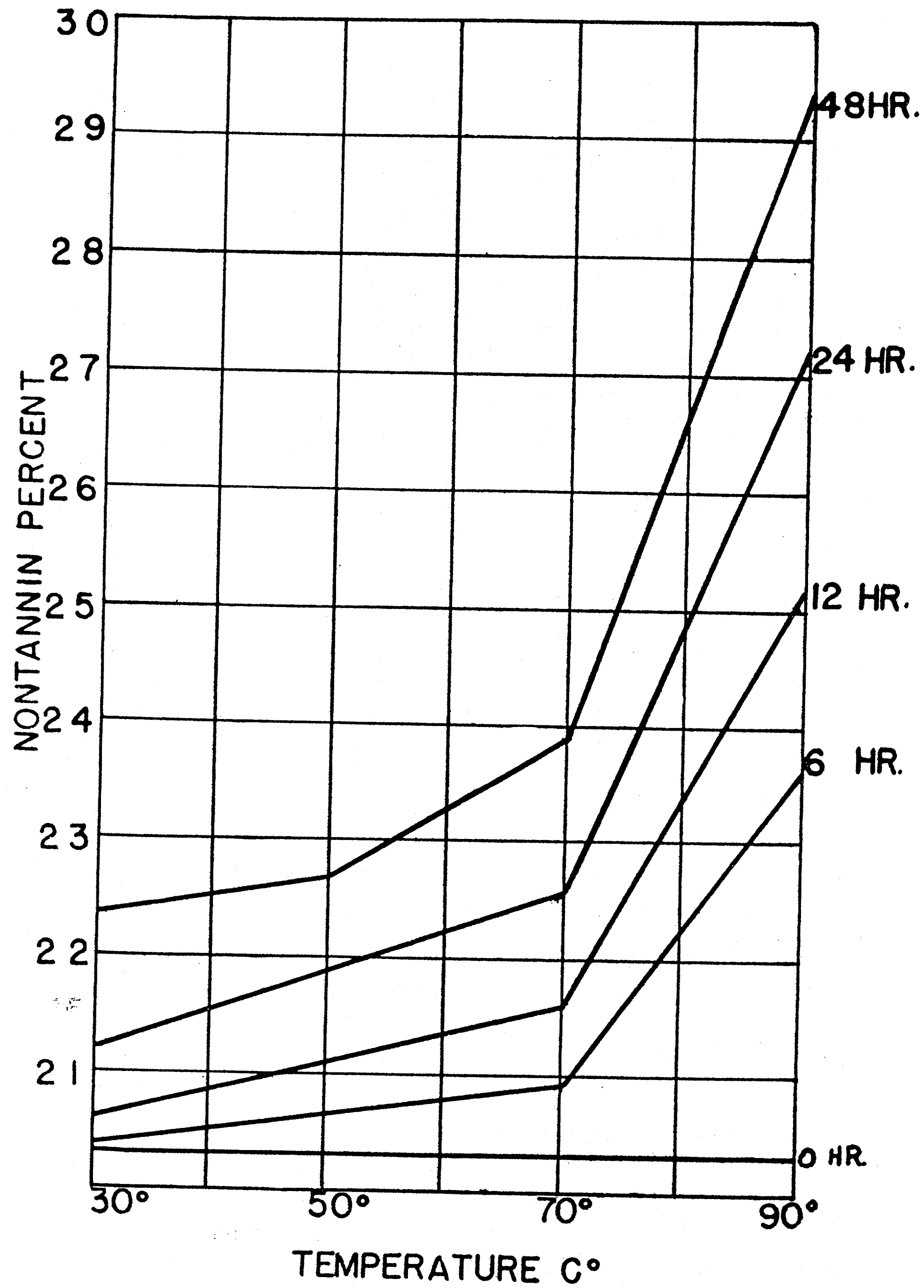

FIGURE III. Variation in non tannin content of sumac leaves with temperature for different periods of time of steeping. Average values for four species of sumac steeped for 6, 12, 24, and 48 hours.

of tannin from combination with another constituent of the leaves. The results for *R. coriaria* are typical of those for the other species.

Below 70° C. the destruction of tannin was moderate, but above this temperature it was rapid. After 6 hours there appeared to be a slight loss of tannin at 70° but none at 50° C. After both 24 and 48 hours there were small losses of tannin at 50° and also at 30 °C. Probably the latter losses were at least partly the result of activity of molds or bacteria.

Non Tannins: Non tannins increased under the conditions that caused a decrease in tannin. Curves in which average percentages of non tannins for the four species have been plotted against temperature are given for each time period in Figure III.

In *R. copallina, R. coriaria* and *R. typhina,* non tannins increased regularly as the steeping conditions became more severe. In *R. glabra,* however, the change was unusual, as may readily be observed from Figure IV. As the temperature was increased from 30° to 90° C. non tannins first showed an increase at 50°, then a decrease between 50° and 70°, and finally a sharp increase between 70° and 90° C. In order to locate the temperature of the minimum point more exactly, portions of leaf material were heated for 24 hours at temperatures of 60°, 70° and 80° C. The results, given in Table VI, indicate that the minimum was between 60° and 70° C. The data as a whole give no information as to the identity of the constituent or constituents responsible for this peculiar behavior.

TABLE VI

EFFECT OF STEEPING IN WATER FOR 24 HOURS AT 60°, 70° AND 80° C. ON THE COMPOSITION OF *Rhus Glabra* LEAFLETS

Determination	Temperature		
	60° C.	70° C.	80° C.
Insolubles, %	1.6	2.2	2.5
Soluble solids, %	49.3	48.2	49.2
Non tannins, %	22.0	22.0	23.8
Tannin, %	27.3	26.8	25.4
Purity of extractive*, %	55.3	55.0	51.6
Reducing sugar, %	4.1	4.1	4.2
Non-reducing sugar, %	1.1	1.3	1.5
Total sugar, %	5.2	5.4	5.7

*Purity of extractive is 100 times the tannin value divided by soluble solids.

Soluble Solids: Soluble solids showed only slight changes, as compared with those in the two constituents of which they are composed, namely, tannin and non tannins. The greatest range in soluble solids was in *R. typhina,* for which a low value of 49.3 per cent and a high value of 53.9 per cent were found, the former in the portion heated at 50° C. for 12 hours and the latter in the portion heated at 90° C. for 48 hours.

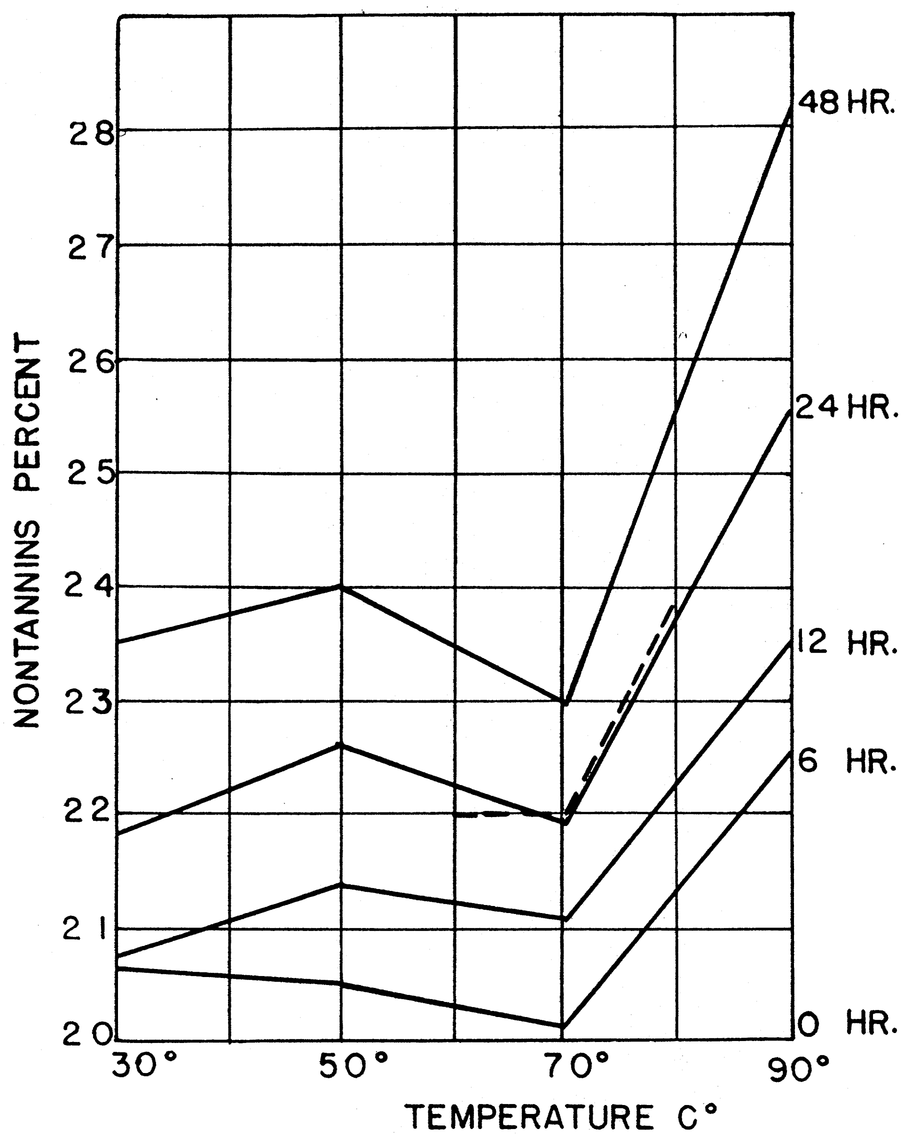

FIGURE IV. Variation in non tannin content of *R. glabra* leaves with temperature for periods of time of steeping.

TABLE VII

Effect of Variations in Time and Temperature of Steeping on the Composition of Leaves of *Rhus copallina* and *Rhus glabra*

Results on Moisture-Free Basis

Temperature of Heating	Time of Heating	*Rhus copallina* Insolubles	*Rhus copallina* Soluble Solids	*Rhus copallina* Non Tannins	*Rhus copallina* Tannin	*Rhus copallina* Purity of Extractive*	*Rhus copallina* pH of Soluble Solids	*Rhus glabra* Insolubles	*Rhus glabra* Soluble Solids	*Rhus glabra* Non Tannins	*Rhus glabra* Tannin	*Rhus glabra* Purity of Extractive*	*Rhus glabra* pH of Soluble Solids
°C.	Days	%	%	%	%	%		%	%	%	%	%	
Room†	0	1.2	51.8	21.7	30.1	58.1	3.6	1.5	45.3	20.0	25.3	55.8	4.1
"	1	1.1	52.1	22.0	30.1	57.8	3.6	1.2	45.9	21.1	24.8	54.0	4.0
"	3	1.1	51.2	22.5	28.7	56.1	3.6	1.1	46.2	24.1	22.1	47.8	3.9
"	5	1.2	51.5	23.2	28.3	55.0	3.5	1.1	45.8	26.0	19.8	43.2	3.9
50	0	1.2	51.8	21.7	30.1	58.1	3.6	1.5	45.3	20.0	25.3	55.8	4.1
"	1	1.4	51.6	22.4	29.2	56.6	3.6	1.5	45.4	21.6	23.8	52.4	4.0
"	2	1.5	51.9	22.8	29.1	56.1	3.6	1.4	46.2	22.7	23.5	50.9	4.0
"	3	1.4	51.7	22.9	28.8	55.7	3.6	1.2	46.6	23.6	23.0	49.4	3.9
"	5	1.3	51.9	23.4	28.5	54.9	3.5	1.1	46.7	25.3	21.4	45.8	3.9
70	0	1.3	52.3	21.9	30.4	58.1	3.6	1.2	45.4	19.7	25.7	56.6	4.3
"	1	1.7	51.5	23.1	28.4	55.1	3.6	1.6	45.0	21.4	23.6	52.4	4.1
"	2	1.8	51.6	23.8	27.8	53.9	3.5	1.8	45.1	22.3	22.8	50.6	4.1
"	3	1.9	51.5	24.5	27.0	52.4	3.5	1.7	45.5	23.0	22.5	49.5	4.1
"	5	2.0	51.3	25.3	26.0	50.7	3.5	1.9	45.4	24.0	21.4	47.1	4.0
90	0	1.4	52.3	22.1	30.2	57.7	3.8	1.2	45.1	19.8	25.3	56.1	4.1
"	1	2.8	52.2	26.8	25.4	48.7	3.6	2.7	46.6	25.4	21.2	45.5	3.7
"	2	3.0	52.1	28.8	23.3	44.7	3.5	2.9	47.9	27.7	20.2	42.2	3.7
"	3	4.0	52.5	30.0	22.5	42.9	3.5	2.7	48.5	29.2	19.3	39.8	3.7
"	5	3.2	52.0	31.5	20.5	39.4	3.5	2.5	48.9	30.7	18.2	37.2	3.6

*Purity of extractive is 100 times t e tannin value divided by soluble solids.

†Room temperature for the *R. copallina* samples was 21° C.; for the *R. glabra* samples, 26 to 27° C.

In *R. copallina* there was no change in soluble solids caused by any of the conditions used. This means that the large decreases in tannin found under the more severe conditions were exactly compensated for by increases in non tannin; a rather surprising result. A solubilization at the higher temperatures of some leaf constituent not otherwise soluble, with a resulting increase in soluble solids, appears to have occurred to some extent in the other three species. In *R. glabra* there was a minimum in soluble solids at 70° C., corresponding to the minimum in non tannins discussed previously.

Purity: Purity, which is the ratio of tannin to soluble solids, varied in practically the same manner as tannin. Since the range in soluble solids for all four species was only from 47.6 to 53.9 per cent, the value for purity was approximately twice the percentage of tannin in every case.

Sugars: Total and reducing sugars in *R. coriaria* were both constant under all conditions except for a slight increase in reducing sugars at 90° C. after 24 hours. In *R. copallina* and *R. glabra* reducing sugars were higher in material steeped at 30° C. than in the untreated material, possibly as the result of enzyme activity. As stated previously, under this condition more mold developed in these two species than in *R. coriaria* and *R. typhina*. Both total and reducing sugars in *R. copallina, R. glabra* and *R. typhina* increased after 48 hours at 90° C.

The changes in sugars were not examined further because all were small, as compared with the total change in non tannins. Although sugars are a part of the latter, they could influence it to only a slight degree, for the maximum increase in non tannins due to treatment was greater than the total amount of sugar present. Changes in sugars do not explain the irregular behavior of *R. glabra* non tannins.

pH Value: There were practically no changes in pH value except under the most drastic heating conditions, in which case there were slight decreases.

Insolubles: There were significant differences in insolubles between the different species. Significant changes were caused by temperature but not by time variations (Table V). The changes were almost entirely increases in insolubles at 90° C.

Preliminary Series of Tests: The results of the preliminary series (Table VII) are presented for two reasons. In the first place, much longer heating periods were used than in the series discussed above. In addition, the data were obtained on two additional samples, one of *R. copallina* and one of *R. glabra,* collected in different locations from those reported on above.

Notwithstanding the differences in samples, the results are in exact agreement with those given in Tables I and III. In *R. copallina* there was a progressive decrease in tannin, an increase in non tannins, and no change in soluble solids as the temperature and time of heating were increased. Under the same steeping conditions, *R. glabra* showed (1) a decrease in tannin,

TABLE VIII

EFFECT OF VARIATIONS IN TIME AND TEMPERATURE OF STEEPING OF SUMAC LEAFLETS ON THE TRANSMISSION* OF SOLUBLE SOLIDS SOLUTIONS FOR GREEN LIGHT (*546 millimicrons*)

Temperature of Heating	Time of Heating	*R. copallina*	*R. coriaria*	*R. glabra*	*R. typhina*
°C.	Hours	%	%	%	%
30	0	88.0	90.5	81.3	93.0
"	6	84.3	90.9	79.5	91.0
"	12	79.2	90.3	80.0	90.5
"	24	82.6	89.8	82.0	90.8
"	48	84.5	90.6	83.1	91.1
50	0	82.5	90.6	81.5	93.0
"	6	79.3	90.6	82.6	93.1
"	12	82.5	91.0	83.5	92.9
"	24	83.7	90.3	84.5	92.3
"	48	83.1	90.4	86.5	91.6
70	0	87.4	89.5	81.7	92.8
"	6	89.0	90.0	85.2	92.6
"	12	87.4	90.9	86.2	91.7
"	24	88.7	88.2	86.9	90.1
"	48	87.5	86.5	87.8	87.5
90	0	87.1	91.1	81.9	92.8
"	6	87.5	90.1	87.8	89.5
"	12	86.6	86.4	86.8	85.9
"	24	86.3	83.4	87.2	82.7
"	48	84.9	76.4	85.6	82.0

*Compared with distilled water. Cell thickness 5 mm.

(2) no change in soluble solids except for a slight increase at 90° C. for the longer heating periods and (3) a minimum in non tannins at 70° C. for each time period. Apparently *R. glabra* leaves and leaflets show the same behavior during steeping. For neither species was there any evidence of an end point either to the destruction of tannin or to the increase in non tannins under the most drastic conditions used in this work.

Color of Soluble Solids: Color was evaluated on all soluble solids solutions of the final series of tests at three wave lengths with a photoelectric photometer,* and complete transmission curves were obtained for several solutions with a recording spectrophotometer. Since all curves were essentially the same shape, a satisfactory evaluation of the brightness aspect of color should be given by the transmission values for green light (546 milli-

* This instrument is similar to that described by Keane and Brice, *Ind. Eng. Chem., Anal. Ed.* **9**, 258 (1937). The light source used for the present experiments was a type AH-3 mercury lamp, and the wave lengths isolated by filters were 436, 546 and approximately 620 millimicrons, the last being less monochromatic than the other two. The instrument is constructed to measure transmission or apparent reflectance, the latter by 45° incidence and normal viewing, relative to MgO.

microns), and these alone have been recorded in Table VIII. Over the range found for these samples, the relation between concentration of coloring material and transmission of green light is nearly linear, with a decrease in the latter resulting from an increase in depth of color. The results show that as the conditions of steeping became more drastic the color of the soluble solids solutions of *R. coriaria* and *R. typhina* darkened but that of *R. glabra* lightened. The darkest *R. copallina* solutions were those heated at 30° and 50° C.

The differences in color between the various soluble solids solutions were by no means as great as the visual appearance of the total solids solutions had indicated. As the severity of steeping conditions increased, the latter showed a decided darkening, with uniform graduation. When the work was planned, it was not realized that much of this color variation would be removed by filtration, and no attempt was made to measure the color of the total solids. This could not have been done by transmitted light, however, and whether reflectance measurements whould have been satisfactory has not been determined. In extract manufacture, the liquors are not cooled and filtered before concentration; therefore the color of the finished extract would be related to the color of the total solids rather than to that of the soluble solids solution.

Of more importance than the color of the solutions is the color of leather tanned with them. The reflectance for green light (546 millimicrons) of sheepskin skivers tanned with the different total solids solutions is given in Table IX. These values, which were obtained on the photometer used for measuring transmission of the soluble solids solutions (see footnote page 114) represent approximately the lightness of the colors of the skivers. A skiver was tanned with each of the duplicate solutions, and values for both skivers are reported.

Examination of the data show that there was a marked darkening of the skivers as a result of steeping the material used for tanning them and that both time and temperature factors were involved. There was no darkening at 50° C., as compared with 30° C., but there was a slight darkening at 70° C. and a very decided darkening at 90° C. As the time of heating was increased, darkening increased gradually, although in 6 hours the change was negligible for *R. coriaria* and *R. glabra* and slight for the other two species. The greatest differences in lightness for a within-species series of skivers were in those tanned with *R. coriaria* and *R. typhina*. The lightest skivers of the entire group were produced with the unheated material of these two species, and the darkest with material that had been heated at 90° C. for 48 hours.

Owing to the fact that the skivers were undertanned as a result of using the same volumes of total solids solutions for the tanning throughout all tests, the reflectance values for the skivers tanned with material heated at

TABLE IX

EFFECT OF VARIATIONS IN TIME AND TEMPERATURE OF STEEPING SUMAC LEAFLETS ON THE REFLECTANCE* FOR GREEN LIGHT (*546 millimicrons*) OF TANNED SHEEPSKIN SKIVERS

Results of Duplicate Tests

Temperature of Heating	Time of Heating	*R. copallina*		*R. coriaria*		*R. glabra*		*R. typhina*	
°C.	Hours	%	%	%	%	%	%	%	%
30	0	60.4	59.6	64.2	66.6	54.1	56.4	67.9	57.0
"	6	58.0	57.4	67.9	65.1	53.5	56.4	64.8	62.1
"	12	57.5	59.2	65.5	64.5	49.3	52.4	61.9	60.0
"	24	56.5	55.5	64.0	65.5	49.8	48.0	68.2	63.0
"	48	54.5	55.4	63.6	62.1	50.0	52.9	61.8	62.1
50	0	61.5	61.3	68.4	65.8	51.4	49.5	65.7	63.3
"	6	60.7	61.0	69.1	69.1	53.0	52.8	66.2	65.7
"	12	56.5	55.8	66.6	63.8	53.0	52.1	65.4	62.1
"	24	59.5	59.0	61.8	64.9	52.4	51.4	64.4	64.8
"	48	61.0	62.3	60.0	64.5	50.2	50.9	62.5	58.7
70	0	59.5	58.9	67.2	63.6	52.9	50.0	66.3	66.6
"	6	61.6	59.5	64.9	68.1	51.4	51.4	60.7	63.1
"	12	58.0	57.8	62.2	64.5	48.5	47.6	59.2	59.7
"	24	57.5	59.0	57.9	60.4	44.3	....	....	54.9
"	48	56.0	54.0	58.5	56.4	45.0	46.4	48.1	49.7
90	0	59.4	60.9	64.2	66.3	58.6	56.5	64.2	66.3
"	6	56.4	55.7	61.0	61.6	52.7	55.0	52.4	52.8
"	12	51.5	50.7	47.0	51.0	51.1	48.8	47.5	....
"	24	47.9	46.1	41.8	43.1	43.8	43.4	34.5	29.0
"	48	38.3	37.0	29.3	31.1	31.0	30.5	24.0	22.8

*Reflectance versus MgO, 45° incidence, normal viewing.

the higher temperatures are somewhat low. At the time the skivers were tanned, the amount of tannin lost during steeping was not known and so could not be compensated for by increasing the volume of liquor. To determine how undertannage may have affected color, duplicate portions of material of each species were heated with water at 90° C. for 48 hours, as described previously; then the decanted solutions were used for tanning sheepskin skivers. Two skivers were tanned with each solution, one with the volume calculated on the assumption that there had been no loss of tannin and the other with an increased volume based on the tannin values in Tables I to IV inclusive. Reflectance measurements on the tanned skivers are given in Table X (Tests III and IV) along with values from Table IX for control skivers (Test I) and for those tanned with material heated at 90° C. for 48 hours (Test II). The reflectance values for skivers tanned with a low ratio of tannin to skin, Test III, agree reasonably well with those for skivers tanned previously with comparable solutions, Test II, for *R. copallina* and *R. coriaria* but not for *R. glabra* and *R. typhina*, possibly indicating an irregular tanning action by steeped sumac. By increasing the volume to compensate for loss of tannin, there was only a slight improvement in lightness as may be seen by comparing the values for Tests III and IV. It therefore seems improbable that any of the values in Table IX are low by a great amount.

TABLE X

REFLECTANCE FOR GREEN LIGHT (*546 millimicrons*) OF SHEEPSKIN SKIVERS TANNED WITH STEEPED SUMAC LIQUORS OF TWO TANNIN-TO-SKIN RATIOS*

Test	Tannin to Skin Ratio	*R. copallina*	*R. coriaria*	*R. glabra*	*R. typhina*
		%	%	%	%
I	correct†	59.4	64.2	58.6	64.2
	"	60.9	66.3	56.5	66.3
II	low‡	38.3	29.3	31.0	24.0
	"	37.0	31.1	30.5	22.8
III	low§	37.2	35.2	41.4	39.0
	"	39.6	36.2	28.4	25.6
IV	correct#	48.0	33.8	38.7	40.7
	"	41.7	30.6	40.4	39.0

*Tanned with total solids solutions from sumac leaflets steeped in water at 90° C. for 48 hours. Results of duplicate tests.

†Results for unheated control; values from Table IX.

‡Volume of solution for tanning not adjusted for decrease in tannin caused by heating; values from Table IX.

§Volume not adjusted.

#Solutions same as for Test III but volume increased to compensate for loss of tannin as shown by results in Tables I to IV inclusive.

TABLE XI

EFFECT OF HEATING DRY SUMAC LEAFLETS AT 101° C. ON THE CHEMICAL COMPOSITION OF THE EXTRACTIVE

Results on Moisture-Free Basis

Species	Time of Heating	Insol-ubles	Soluble Solids	Non Tannins	Tannin	Sugars			pH of Extrac-tive	Color of Soluble Solids*	Color of Skivers†
						Reducing	Non-Reducing	Total			
	Hours	%	%	%	%	%	%	%	%	%	%
R. copallina	0	1.8	52.3	19.0	33.3	2.8	2.4	5.2	4.0	87.1	60.2
	24	1.8	50.9	18.3	32.6	1.3	2.8	4.1	4.0	84.5	57.5
	48	1.6	50.8	18.1	32.7	1.2	2.7	3.9	4.0	82.1	55.8
R. coriaria	0	1.5	50.5	20.0	30.5	3.5	0.7	4.2	4.2	91.1	65.4
	24	2.1	50.2	20.1	30.1	2.6	1.2	3.8	4.2	88.0	63.2
	48	2.4	49.6	19.7	29.9	2.1	1.5	3.6	4.1	87.6	61.2
R. glabra	0	1.8	48.5	20.2	28.3	3.9	1.8	5.7	4.3	81.9	57.6
	24	2.0	47.8	19.7	28.1	2.6	1.8	4.4	4.2	80.6	54.8
	48	2.7	47.6	19.2	28.4	1.7	2.1	3.8	4.2	78.8	51.4
R. typhina	0	1.2	49.8	22.7	27.1	5.0	1.4	6.4	4.4	92.8	65.2
	24	2.1	49.6	23.1	26.5	1.9	3.3	5.2	4.3	88.0	55.5
	48	1.8	49.6	22.6	27.0	1.8	3.1	4.9	4.3	87.9	52.5

*Percentage transmission for green light (546 millimicrons), as compared with distilled water. Cell thickness 5 mm.

†Percentage reflectance for green light (546 millimicrons) of sheepskin skivers tanned with total solids solutions. (See footnote *, Table IX).

The skivers from Test IV were not only dark in color but they were also thin, "papery," and in no way equal to those tanned with unheated material (Test I). Steeping at high temperatures, therefore, not only resulted in the formation of substances that produce dark leather, but also affected the ability of the steeped material to combine with skin or hide substance. Purity of the extractive from the steeped material was low, but whether the poor fixation of tannin was caused by low astringency or by some alteration of the tannin molecule could not be determined from the data obtained.

Effect of Dry Heat: Heating for either 24 or 48 hours at 101° C. in the dry state before extracting for analysis resulted in relatively small changes in most constituents (Table XI). The change occurred principally during the first 24 hours of heating, the change during the second 24 hour heating period being generally smaller.

An analysis of variance (Table XII) shows that in all analytical values heating caused changes that were significantly greater than the experimental error. Interactions for species with soluble solids, non tannins and tannin were not significant, so these constituents changed in about the same manner in all four species. Insolubles increased except in *R. copallina.* Non tannins and tannin of *R. copallina* and *R. coriaria* and non tannins of *R. glabra* showed slight tendencies to decrease during heating in the dry condition, but the decreases were not pronounced.

The most noticeable changes were in sugars. Reducing sugars decreased

TABLE XII

ANALYSIS OF VARIANCE OF ANALYTICAL RESULTS FOR FOUR SPECIES OF SUMAC HEATED AT 101° C. FOR 0, 24 AND 48 HOURS

Source of Variation	Species	Time	Interaction: Species x Time	Error
Degrees of freedom	3	2	6	12
Insolubles, mean squares	0.2890**	0.6549**	0.2035**	0.0347
Soluble solids, mean squares	11.5547**	1.6582**	0.2381	0.1556
Non tannins, mean squares	20.2092**	0.7356**	0.0087	0.0464
Tannin, mean squares	40.2602**	0.5015**	0.0910	0.0532
Reducing sugars, mean squares	1.6083**	9.8964**	0.5483**	0.0176
Nonreducing sugars, mean squares[1]	3.0793**	1.3461**	0.3836**	0.0156
Total sugars, mean squares	2.8422**	4.0168**	0.1771**	0.0151
pH, mean squares	0.1131**	0.0078**	0.0017*	0.0004
Color of skiver, mean squares	78.34**	96.06**	9.96*	3.00

[1] Eleven degrees of freedom for error because of one missing value.
* Significant at 5 per cent point.
**Significant at 1 per cent point.

markedly; nonreducing sugars increased to a somewhat less degree, with the result that there was a moderate net decrease in total sugars. This decrease in total sugars was greater than the decrease in non tannin, although sugar is a part of the latter. Dry heat apparently changed part of the sugar to a soluble non-sugar or at least altered it so that it was no longer able to reduce Fehling's solution after acid hydrolysis.

A pronounced darkening of both the soluble solids solutions and skivers tanned with the total solids solutions was caused by dry heat.

Summary

The effects of time and temperature of steeping on the composition of sumac leaves and leaflets and on the color of leather tanned with them were studied. Sicilian sumac *(Rhus coriaria)* and three species of domestic sumac *(R. copallina, R. glabra* and *R. typhina)* were used. Four temperatures were tested, namely, 30°, 50°, 70°, and 90° C. The time periods were 1, 2, 3, and 5 days in a preliminary series of tests on *R. copallina* and *R. glabra,* and 6, 12, 24, and 48 hours in a final series of tests on all four species.

Sumac leaves, while steeping in water, decreased in quality. This was indicated by a decrease in tannin content, an increase in non tannins about equal to the decrease in tannin, and the production of darker colored skivers. The quality became proportionally lower as either time or temperature of steeping increased. No end point to either the destruction of tannin or increase in non tannins was evident after steeping at 90° C. for 5 days. The only irregularity was a minimum in non tannins in *R. glabra* at 70° C., the cause for which was not determined. The changes apparently began as soon as water was added to the leaves, although at 30° C. they were very slight and for the longer time periods they were overshadowed by changes due to bacterial action. The rate of destruction of tannin was considerably slower below 70° C. than it was above this temperature. For example, at 50° C. there was a negligible loss in 6 hours, but at 90° C. there was an appreciable loss of tannin in only 2 or 3 hours. Because the destruction of tannin is continuous and the effects of time and temperature are interdependent, it is not possible to set time and temperature limits for commercial leaching. The manufacturer must keep these factors low enough to obtain a product of good quality but high enough for profitable leaching efficiency.

Steeping increased reducing sugars moderately and total sugars slightly, but under conditions suitable for commercial leaching the changes in sugars would not affect the character of the extract.

Prolonged steeping lessened the ability of sumac to tan sheepskins.

Dry heat destroyed sugars but had little effect on tannin. This is the reverse of the effect of steeping, showing that water plays an important role in determining the type of change that sumac leaves undergo during heating.

References

1. American Leather Chemists Association. By-laws and Methods of Sampling and Analysis. 1940.
2. Clarke, I. D., and Frey, R. W. An Efficient Installation for the Laboratory Extraction of Tanning Materials. *J.A.L.C.A.*, **38,** 178 (1943).
3. Frey, R. W., and Clarke, I. D. An Improved Reed-Churchill Extractor. *ibid.*, **34,** 614 (1939).
4. Parker, J. Gordon, and Gilman, J. A. Influence of Temperature on the Tannin Yield of Pyrogallol Tans. *J.I.S.L.T.C.*, **11,** 374 (1927).
5. Parker, J. Gordon, and Procter, H. R. The Effect of Different Temperatures in the the Extraction of Tanning Materials. *J.S.C.I.*, **14,** 635 (1895).
6. Parker, J. Gordon, and Winch, L. Extraction of Sumac for Analysis. *J.I.S.L.T.C.*, **10,** 272 (1926).
7. Riethof, O. Color Tests with Skivers. *J.A.L.C.A.*, **11,** 2 (1916).
8. Snedecor, G. W. Statistical Methods. The Iowa State College Press. 1940.